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COKE DISSOLUTION IN LIQUID IRON - THE EFFECT OF COKE MINERAL MATTER

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Abstract

Metallurgical coke, the primary fuel of the ironmaking blast furnace contains approximately 8-12% mineral matter and carbon. The formation and development of the mineral matter layer that formed between coke and liquid iron during carbon dissolution has been investigated. Coke particles (-2mm, +0.5mm) were added to the top surface of an iron 2 mass% C melt at representative ironmaking temperatures of 1450°C, 1500°C and 1550°C, for periods of time between 2 minutes and 120 minutes, before being quenched. The samples were then sectioned and the coke-iron interface examined in the SEM. The mineral matter layer that formed during the dissolution of carbon from coke into liquid iron has been found to form a solid layer of calcium aluminates at the coke-metal interface. The composition and morphology of these calcium aluminates was observed to change over time, changing from an open acicular structure to a dense structure. The change in the composition and morphology of these aluminates was also observed to have a significant role in determining the rate of the coke(carbon) dissolution. The changes observed in the rate can be directly attributed to the densification of the interfacial mineral layer impeding iron's contact with the coke. In the ironmaking blast furnace this densification of a mineral matter layer will reduce the efficiency of the ironmaking process by prohibiting the dissolution of coke. By understanding this process ironmakers can optimise coke usage in the blast furnace, reducing coke consumption, operating costs and emissions of CO₂.

Introduction

Coke is a critical reagent in the production of blast furnace iron. It is the furnace fuel, enabling the furnace to achieve the high temperatures required for economic iron production, it dictates the flow distribution within the furnace, and is the source of carbon in the liquid iron product [1]. This investigation is focused on the coke/metal reactions occurring in the hearth below the slag layer. Liquid iron entering this region contains around 2 mass%C, and picks up more than half of its final carbon while percolating through the packed coke bed in this region[1]. Metallurgical coke typically contains 8-12% by mass inorganic mineral matter[2]. As coke is dissolved in the liquid iron, there is potential for the insoluble components of this inorganic mineral matter to form a layer at the surface of the coke inhibiting carbon dissolution[3-10]. This inorganic mineral matter is often referred to as ash in coke dissolution studies.

There is a significant body of research that has focused on the kinetics of coke dissolution into iron[4, 7-9, 11, 12]. Coke dissolution into iron is generally considered to be controlled by first order kinetics and is frequently described by the rate of carbon dissolution if liquid phase mass transfer limits the dissolution reaction. Assuming A , V and k_m are constant, liquid phase mass transfer can be represented by equation 1.

$$\frac{V}{A} \ln \left(\frac{[C]_{\text{sat}} - [C]_0}{[C]_{\text{sat}} - [C]_{\text{bulk}}} \right) = -k_m t \quad (1)$$

The role ash plays in reducing the rate of carbon dissolution into iron from coke has been reported by several researchers[4, 7, 9]. Gudenau et al[4] indicated that an ash film formed on the surface of the coke, and that presence of this film was significant in reducing the rate of carbon dissolution from the coke. In this study it was found that the addition of refractory oxides, CaO, MgO, Al₂O₃ to the coke further decreased the dissolution rate, while additions of iron oxide enhanced the dissolution rate.

Orsten and Oeters[7] reasoned that a solid ash product would be distributed across the reaction surface, reducing the available contact area between the carbonaceous material and the melt, however, if the ash product was liquid, it could be flushed away from the interface, reducing this effect.

Utilising a sessile drop apparatus to react a drop of iron with a carbonaceous substrate, Wu et al[10], McCarthy et al[6] and Khanna et al[5], reported on the presence and composition of the ash product at the droplet / carbonaceous material interface. General observations of the droplet surface in these studies indicate that although silica was contained in the carbonaceous material, there was none present in the ash at the interface. The ash at the interface was initially Al₂O₃, however as the reaction time increased, the proportion of CaO increased, after which the Al₂O₃ was observed to disappear from the droplet-coke interface and was replaced by an iron calcium sulphide. Khanna et al[5] also observed a significant change in the rate of carbon dissolution over time in some chars. Chars with high CaO levels displayed a two stage behaviour, whereby after a period of time the rate of dissolution would decrease significantly. This two stage behaviour was attributed to the increased deposition of calcium based reaction products blocking the reaction surface.

In a recent study by the current authors[3], examination the coke-iron interface of coke samples immersed in liquid iron showed that the type of mineral layer formed was temperature dependant. Further it was found, consistent with the work in this area[5, 6, 10], that SiO₂, although the largest single component of the mineral matter in the unreacted coke was essentially absent from the predominately Al₂O₃ / CaO coke-iron mineral layer. The formation of the layer was described in terms of a temperature activated time dependant sintering/fusion mechanism.

There has been no definitive study published in the literature that has characterised the development of the mineral matter layer with time and temperature and its affect on the coke (carbon) dissolution. Characterising the mineral layer's development is the focus of this study and the experimental results presented in this paper.

Experimental

A series of coke (carbon) dissolution experiments were conducted whereby 35g of crushed coke (-2mm + 0.5mm) was added directly to the top surface of 572g of liquid iron 2mass% carbon alloy. The melt was frequently sampled with a 1mm ID quartz tube over a period of 2 hours. A second series of quenched coke (carbon) dissolution experiments were performed whereby 10g of crushed coke (-2mm + 0.5mm) was added directly to the top surface of 164g of liquid iron 2 mass% carbon alloy. The melt plus coke were held at temperature for a period of time ranging from 2 to 120 minutes. At the end of this time, the crucible containing the melt and coke was quenched by lowering it into a water cooled stainless steel quenching chamber fitted to the bottom of the furnace. After quenching the samples were sectioned and prepared for electro-optical examination. Both series of experiments were conducted in resistance heated vertical tube furnaces under an Ar atmosphere over the same temperature range of 1450-1550°C. The temperatures were chosen to replicate what might be expected in the lower zone deadman area of a blast furnace.

The coke mass was determined such that if sufficient carbon was transferred to the iron melt for it to become carbon saturated there would be a 10mm layer of coke on the iron surface to maintain an excess of carbon. The crucible, iron mass and coke masses used in the quenched series of experiments were determined to maintain the key geometric factors of coke-metal mass ratio and melt mass-surface area ratio. For further details of the experimental technique see Chapman et al[13].

Raw materials

The coke samples used were provided by BlueScope Steel and contained approximately 0.4 – 0.45 mass% sulphur and 11.6 mass% inorganic material. The inorganic material can be considered to be refractory in nature. The lump coke was coarsely crushed to obtain the desired -2mm + 0.5mm size fraction used. A detailed oxide composition measured by XRF after ashing at 815°C is given in Table 1.

Table 1: Composition of the of the oxide components in the coke

Mass %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	P ₂ O ₅	MgO
	54.8	32.3	4.9	2.9	1.42	1.0
Mass %	K ₂ O	TiO ₂	Na ₂ O	S	Mn ₃ O ₄	
	0.51	1.4	0.38	0.063	0.05	

The iron carbon alloy was prepared in situ before the carburiser was added by melting appropriate amounts of electrolytic iron and coarsely crushed spectrographic grade graphite rod to achieve a 2% carbon-iron alloy prior to the addition of the coke.

Sample preparation

The quenched crucible containing the iron alloy and coke was impregnated with liquid resin under vacuum to preserve the coke-metal interface during sectioning. To minimise coke movement during the vacuum impregnation procedure, lead shot was added to the top of the coke inside the crucible, before the resin impregnation. The bottom section of the crucible was removed and iron samples for analysis were machined from the iron block. A vertical cut was made across the centre of the sample exposing the coke-metal interface. The interface was mounted in epoxy resin and prepared for SEM analysis.

Carbon analysis was performed using a LECO CS-444 analyser, other metal analysis was performed by atomic absorption methods.

Results / Discussion

Carbon transfer

Carbon pickup for the quenched and non quenched dissolution experiments, is plotted for 1450°C, 1500°C and 1550°C as a function of time in Figure 1. The dashed line presented in Figure 1 represents both the quenched and non quenched data sets. The good agreement in the level of carbon pickup with time between the two experimental methods employed in this study indicates that the same factors that influence the kinetics of carbon transfer from coke to the iron are active in both sets of experiments.

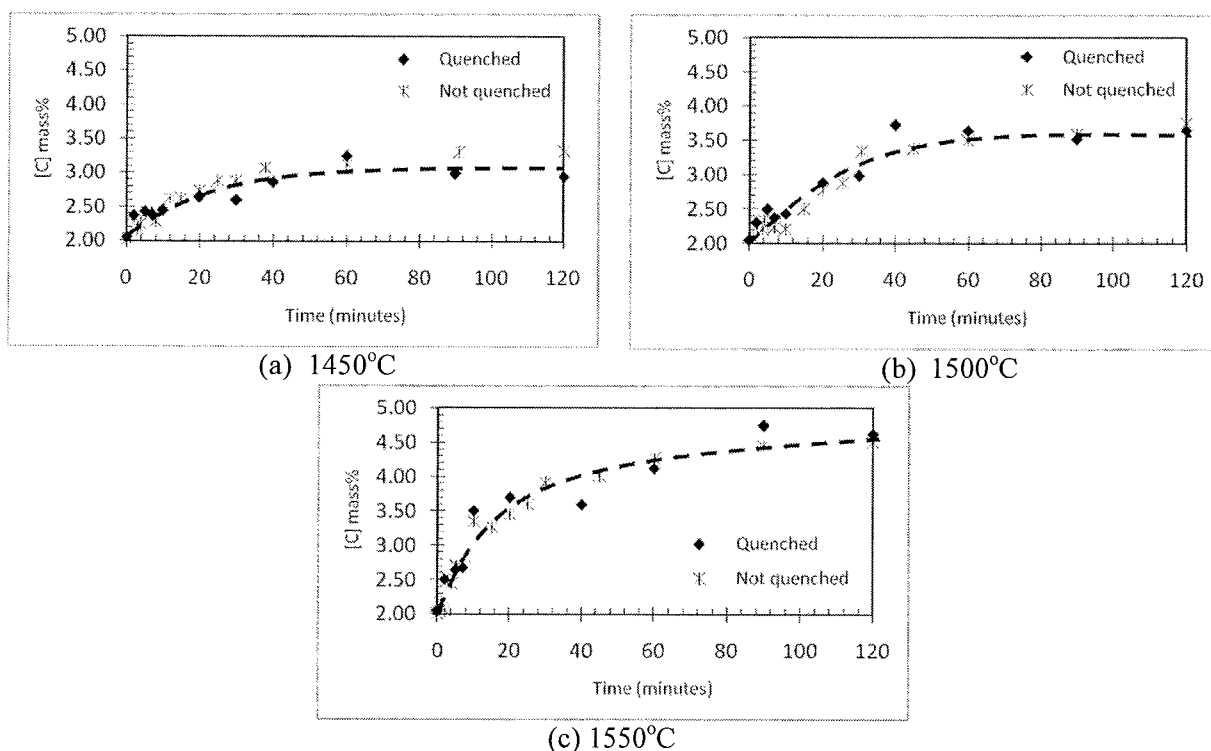


Figure 1 [C] verses time at a) 1450°C, b) 1500°C and c) 1550°C

In the case of the 1450°C and 1500°C quenched carburiser cover results, the carbon level is seen to increase steadily before reaching a maximum of approximately 3.0 and 3.6 mass% at 60 and 40 minutes respectively. Beyond this there was little subsequent carbon pickup in the melt. In the case of the 1550°C quenched carburiser cover results, the carbon pickup was initially rapid, and although no clear plateau is observed the rate of carbon transfer to the melt slowed, with the carbon reaching a maximum of approximately 4.67 mass% after 120 minutes of contact. The maximum carbon levels reached in these experiments are significantly below the carbon saturation levels calculated using MTDATA[14] of 5.09, 5.20 and 5.32 mass% carbon respectively.

Layer formation and development

The following results are observations and measurements obtained from the quenched series of experiments, and are of the coke-iron interface after quenching. Unless otherwise stated, it is assumed that the results are representative of the high temperature phenomena. Mineral matter compositions where reported, are derived from EDS analysis of the quenched samples. A more detailed analysis of the mineral compositions is given elsewhere[13].

Evidence of a mineral layer was observed in all samples at all experimental times from 2 minutes to 120 minutes over the 3 experimental temperatures of 1450°C, 1500°C and 1550°C. A typical section of quenched interface after 5 minutes at 1500°C is presented in Figure 2. The mineral layer is observed following the profile of the iron surface. The original liquid iron surface is observed to have contracted away from the mineral layer. The resulting voids are filled with resin during the metallographic preparation of the sample.

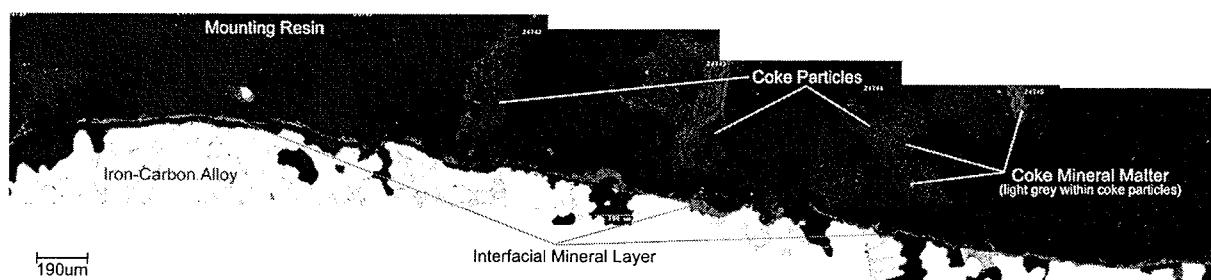


Figure 2 SEM Backscattered electron images of the quenched coke-metal interface, quenched after 5 minutes at 1500°C.

The composition of the mineral layer was found to be principally composed of calcium and aluminium oxides. The ratios of calcium and aluminium found in the mineral layer indicate that the mineral layer is composed of alumina, and the calcium aluminates, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The melting points of these phases are well above the experimental temperatures [15]. There was no evidence of the quenched mineral layer being liquid at the experimental temperatures. Therefore it is assumed the original mineral layer was solid before quenching and the original solid structure and composition of the mineral layer is retained in the quenched sample.

The amount of material present in the mineral layer between the coke and liquid iron was observed to be increasing with reaction time. As the coke dissolution reaction continues the predominant structure changes from a loose agglomeration of primarily alumina particles to an open porous network of acicular needles as shown in Figure 3. These needles are predominately CA6, containing up to approximately 9 mass% CaO. On further dissolution the calcium enrichment of the mineral layer continues. The layer retains a relatively open

structure however the fine needles evident in Figure 3 are replaced by a coarser structure as 2 dimensional plates of CA2 develop. As the dissolution reaction continues further, the calcium enrichment of the mineral layer also continues. CaO levels are observed reaching in excess of 25 mass%. The structure of the predominant mineral layer changes from being an open structure evident in Figure 3 to a dense CA2-CA layer that is well bonded to the iron surface as shown in Figure 4.

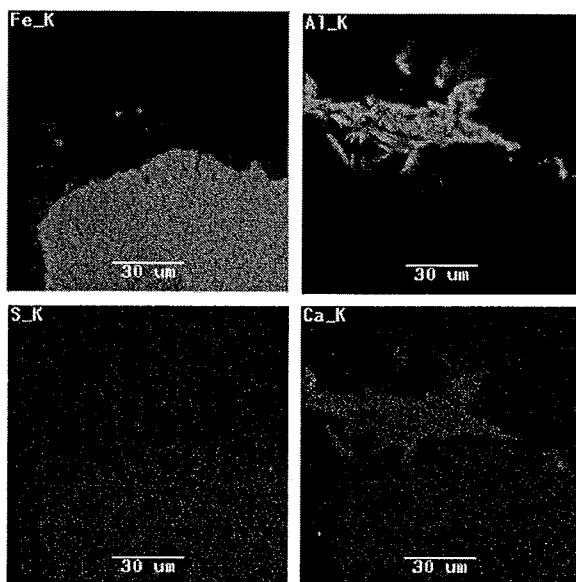
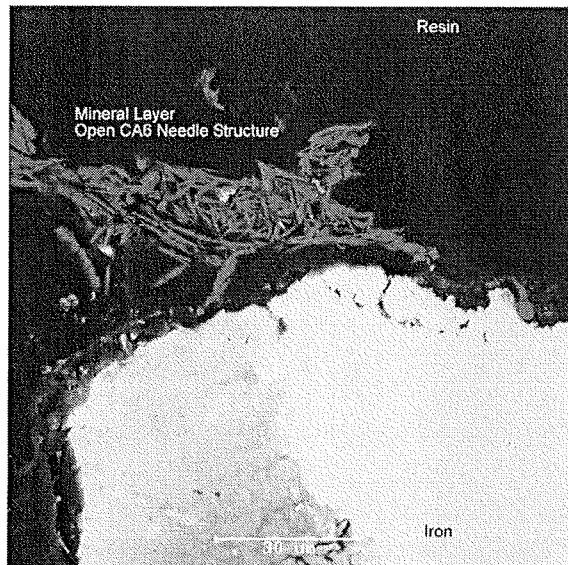


Figure 3 SEM Backscattered electron images and elemental X-ray maps of mineral matter layer quenched after 2 minutes at 1500°C.

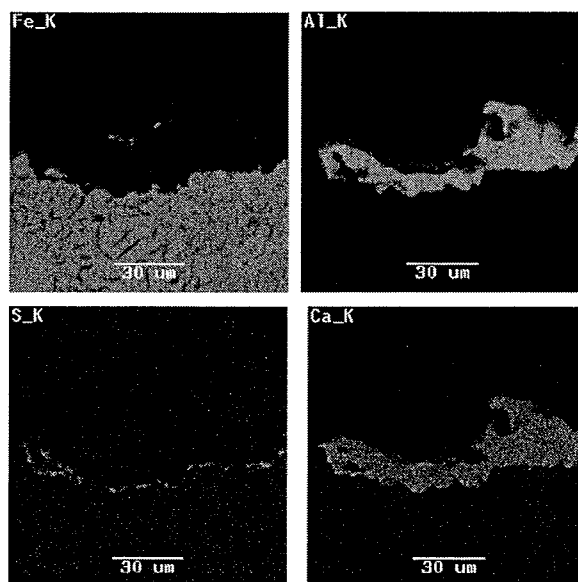
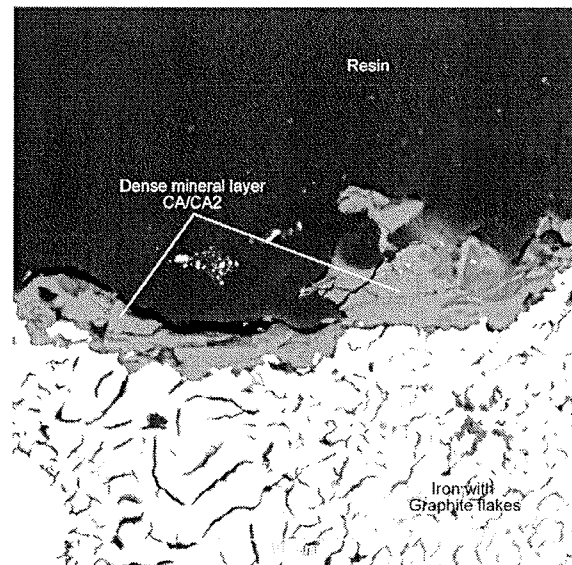


Figure 4 SEM Backscattered electron images and elemental X-ray maps of mineral matter layer quenched after 60 minutes at 1500°C.

The role of calcium enrichment in the mineral layer at the melt interface can be understood by considering the CaO-Al₂O₃ binary phase equilibria [15]. There are three distinct calcium aluminates at the alumina rich end of this system (below 1600°C). The structures of these calcium aluminates are given in Table 2.

Figure 5(a) details the development of the coke-iron mineral layer in terms of its molar CaO-Al₂O₃ ratio. From Figure 5(a) it can be seen that calcium present in the mineral layer increases with temperature and reaction time.

Combining the information presented in Figure 5(a), the calcium aluminate data presented in Table 2 and knowledge of the CaO-Al₂O₃ phase equilibria (below 1600°C)[15], the predominant calcium aluminate phases present in the coke-iron interfacial mineral layer can be represented as shown in Figure 5(b).

Table 2 Structure of the alumina-rich calcium aluminates.

Phase	Abbreviation	Molar CaO/Al ₂ O ₃ ratio	Typical Structure[16]	Melting Point[15]
CaO.6Al ₂ O ₃	CA6	0.16	Acicular needles	1830°C
CaO.2Al ₂ O ₃	CA2	0.5	Plate like crystals / Needles	1762°C
CaO.Al ₂ O ₃	CA	1.0	Dense fine grains	1602°C

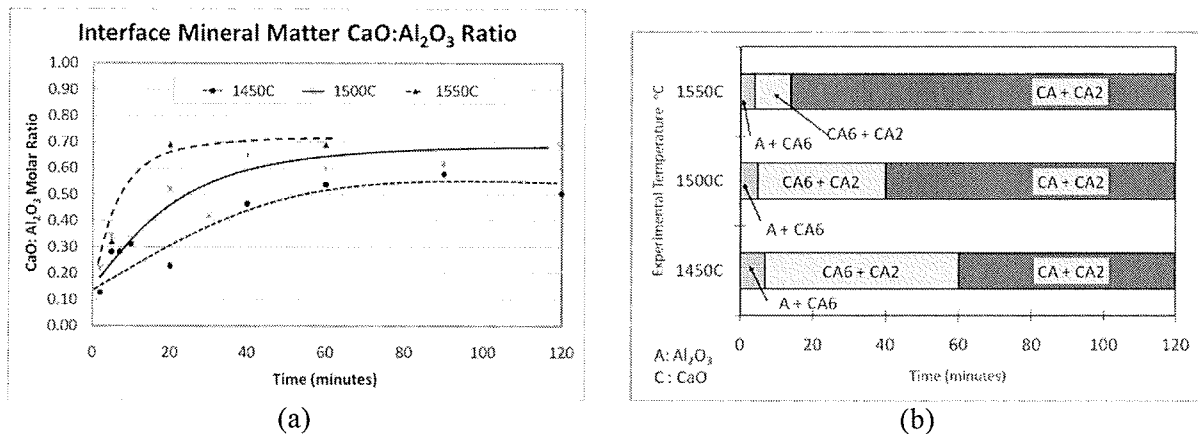


Figure 5 a) Molar CaO-Al₂O₃ ratio verses experimental time. b) Predominant mineral matter phase(s) at the coke – metal interface verses experimental time.

Carbon dissolution kinetics

Coke dissolution into iron is considered to be a first order kinetic process and is generally described as being limited by liquid phase mass transfer of carbon in iron. The mass transfer coefficient, k_m , for such a process can be evaluated as the slope of a plot the left hand side of equation 1 verses time. Such plots are given in Figure 6.

In Figure 6, it can be seen that there is a significant change in k_m , the rate constant, after a period of time for all three temperatures. The change in k_m , a decrease in the slope, represents a slowing of the rate of coke (carbon) dissolution into the iron. At the lower temperatures of 1450°C and 1500°C after approximately 60 and 40 minutes respectively, the dissolution reaction effectively stops. At 1550°C, although the change in the rate constant is not as pronounced, it still represents a significant slowing of the carbon dissolution reaction. The change in k_m has been interpreted as a change in the kinetic regime controlling the dissolution of carbon from the coke.

Effects of structure on kinetics

The change in the rate constant is coincident with the change in the predominant phases present in the mineral layer at the coke-iron interface from CA2/CA6 to CA/CA2. This change in phase is accompanied by a change in the morphology of the mineral layer from an

open acicular structure to a more densely packed structure. This change in the morphology reduces the contact between the carbon in the coke and the liquid iron, and therefore slows the rate of coke (carbon) dissolution. While other workers have inferred that the nature of the mineral layer that could form at the coke-iron interface will affect the kinetics of the carbon dissolution reaction[4-6, 9, 10]. This investigation demonstrates for the first time that the composition and subsequent morphology of the mineral layer formed affects the carbon dissolution reaction. In the absence of a mineral (product) layer carbon dissolution into iron is considered to be a first order liquid phase mass transfer process[4, 7-9, 11, 12]. In stating that the nature of the mineral layer formed during the coke dissolution affects the kinetics of the carbon dissolution reaction, a change in the reaction control mechanism is implied. Assuming that mass transfer of carbon in the liquid iron is still in part rate controlling, the formation of the mineral (product) layer provides an additional controlling mechanism. This represents a change from simple mass transfer control to a mixed control regime where both mass transfer and the mineral (product) layer are active. Further, the changing nature of the mineral layer from open to dense structure could also be interpreted as a change in the reaction control mechanism.

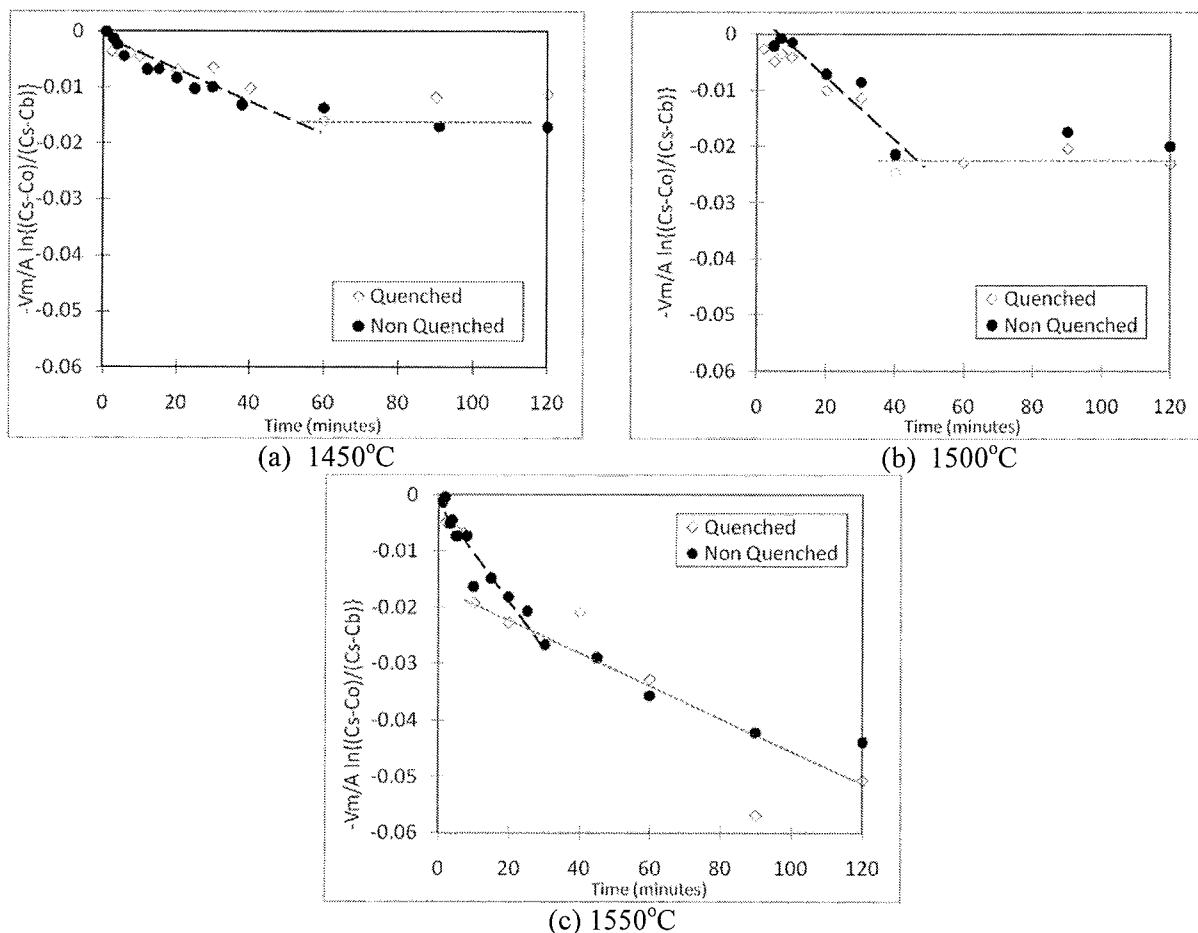


Figure 6 First order mass transfer control plots for a) 1450°C, b) 1500°C and c) 1550°C.

Calcium enrichment of the mineral matter layer

Calcium enrichment of the mineral matter at the melt interface is a key component of the formation of the mineral layer and its subsequent densification. Calcium enrichment levels are well above what should be expected solely from coke dissolution. Calcium levels in the iron melt have been measured throughout the experiment and were found to have changed from 24

± 1 ppm calcium initially to 22 ± 1 ppm calcium after 120 minutes. A 10% increase in the molar $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of the mineral layer would be achieved by a loss of 2.6ppm calcium from the iron. Therefore although the change in the experimental calcium level is significant, it does not fully explain the calcium enrichment of the mineral layer observed. Other workers have reported calcium mobility within coke[17, 18] while calcium enrichment at the melt interface has been reported by other researchers[3, 5, 6, 10]. This offers the possibility that enrichment of the mineral layer is also a result of calcium mobility within the coke. From the results reported it is not possible to distinguish between calcium in the mineral layer originating from the coke and the calcium from originating from the iron melt.

Conclusions

A series of experiments has been carried out in an attempt to describe and characterise the mineral layer formed at the coke-metal interface as the coke dissolved into the liquid iron. It was found that

- The kinetics of carbon dissolution from the coke to the liquid iron were dependant on the structure of the interfacial mineral layer.
- The changing morphology of the mineral layer was directly related to compositional changes, with calcium enrichment of the mineral layer dictating the predominant phase and thus morphology of the mineral layer.
- The formation of the mineral (product) layer was interpreted as an additional rate controlling mechanism for the coke (carbon) dissolution reaction. This represents a change from simple mass transfer control to a mixed control regime where both mass transfer and the mineral (product) layer are active.

Acknowledgments

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List of symbols

D = Diffusion coefficient of carbon in liquid iron ($\text{m}^2.\text{s}^{-1}$)	J = Flux (composition. $\text{m}.\text{s}^{-1}$)
$[C]_{\text{sat}}$ = Carbon concentration at carbon saturation (mass %)	V = Volume of melt (m^3)
$[C]_{\text{bulk}}$ = Bulk carbon concentration in melt (mass %)	A = Area of reaction interface (m^2)
$[C]_0$ = Initial carbon concentration of bulk at $t=0$ (mass %)	t = Time (s)
δ = Effective boundary layer thickness (m)	k_m = Mass transfer coefficient ($\text{m}.\text{s}^{-1}$)

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